Soap-Based Detergent Formulations: II. Oxyethylated Fatty Amides as Lime Soap Dispersing Agents[1]

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ABSTRACT

Nonionic surface active agents with two oxyalkyl chains were prepared from the triethylamine catalyzed reaction of ethylene oxide with diethanolamides of palmitic, stearic and tallow fatty acids. The addition of 4 moles of ethylene oxide was required to render these diethanolamides water soluble, whereas 9 moles were required to make the corresponding monoethanolamide soluble. Efficiency of lime soap dispersion increased as oxyethyl chain length was increased. Best detergency of soap-nonionic combinations was achieved when the oxyethyl chain length was at the minimum required for water solubility. The γ-hydroxyethanolamides and -diethanolamides were prepared by the uncatalyzed reaction of the corresponding amines with γ-stearolactone. These compounds became water soluble at lower levels of oxyethylation, but the lime soap dispersing power and detergency were not improved over those of corresponding compounds derived from stearic acid.

INTRODUCTION

Nonionic surface active agents are known to be among the most effective lime soap dispersing agents (1). Their use in combination with soap has frequently been suggested in the patent literature, but the results of detergency tests have usually been disappointing (2). The probable cause is that the excessive bulk of the nonionic hydrophile blocks the anionic function of the soap at the surface, thus causing the mixture to take on the properties of a nonionic surfactant. If adequate water solubility and lime soap dispersing power could be achieved without excessive bulk, the product might be expected to formulate well with soap. The work reported here represents a study of the effects of one and two oxyalkyl chains of varying chain length on solubility, lime soap dispersing power, and detergency. Ethanolamides and diethanolamides were used as starting materials for oxyethylation. Knaggs has shown that oxyethylation of amides or ethanolamides leads to the growth of a single oxyalkyl chain (3). Thus the preparation of amides with two oxyalkyl chains had to start with dialkanolamides. Oxyalkylations were carried out using the mild conditions described by Carnes (4), to minimize isomerization of amide to ester.

[1]Presented at the AOCS Meeting, Los Angeles, April 1972.
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EXPERIMENTAL PROCEDURES

Alkanolamides

Ethanolamides were prepared by amidation of methyl

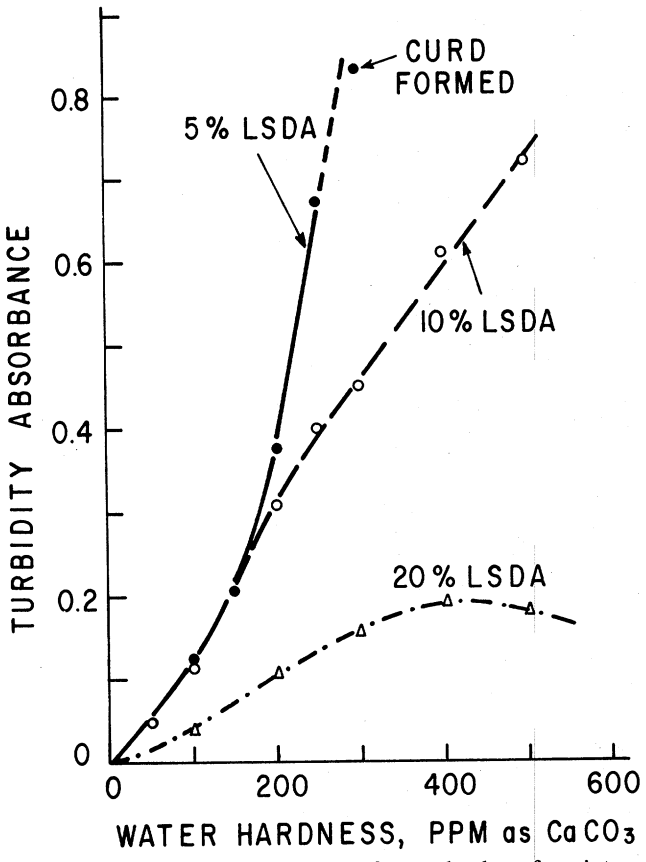

FIG. 1. Turbidities as a function of water hardness for mixtures of soap with diethanoltallowamide + 4.6 moles of ethylene oxide (LSDA).

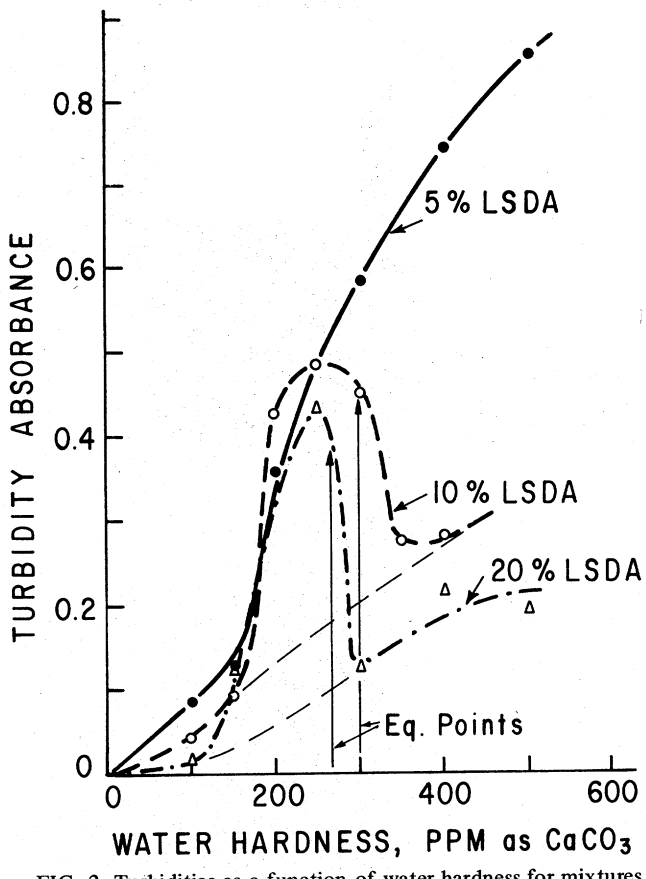

FIG. 2. Turbidities as a function of water hardness for mixtures of soap with diethanoltallowamide + 10 moles ethylene oxide (LSDA).

TABLE I

Detergency of Oxyethylated Amides

Lime soap dispersing agent (LSDA)	Lime soap dispersing power,[a] %	Detergency, ΔR[b]								
		0.05% LSDA			0.128% Tallow soap +0.042% LSDA +0.030% Silicate[d]					
		300 ppm			150 ppm			300 ppm		
		A[c]	B[c]	C[c]	A	B	C	A	B	C
Diethanolpalmitamide										
plus 3.0 EO	9	4.6	24.8	6.8	37.0	35.8	5.8	16.3	22.6	7.2
plus 5.0 EO	8	7.1	28.4	6.8	34.4	26.6	3.8	17.2	26.6	6.2
plus 10.0 EO	3	7.0	17.0	3.4	33.9	13.1	2.8	17.6	16.4	3.4
Diethanolstearamide										
plus 2.9 EO	12	5.4	19.0	9.7	37.7	33.2	5.8	15.8	27.4	8.8
plus 4.6 EO	9	6.2	26.9	6.3	36.2	29.6	5.3	15.6	25.2	7.1
plus 7.6 EO	6	6.8	20.1	3.2	36.8	18.0	3.8	17.2	19.6	5.8
plus 11.0 EO	3	7.1	16.1	3.4	37.2	17.2	2.8	15.2	19.2	5.2
plus 14.0 EO	2	7.0	14.3	2.4	35.9	16.5	2.4	18.3	18.6	6.9
Ethanolstearamide										
plus 9.0 EO	9	6.8	24.6	3.4	35.8	30.6	5.1	16.4	22.4	3.2
plus 11.2 EO	3	6.6	21.6	2.7	35.6	22.2	3.6	17.4	25.4	4.2
γ-Hydroxy ethanolstearamide										
plus 5.0 EO	9	7.0	20.6	6.6	39.5	36.5	9.0	20.4	23.4	6.1
plus 9.2 EO	7	7.9	14.9	7.6	36.5	25.2	7.8	23.0	21.6	5.8
γ-Hydroxy diethanolstearamide										
plus 2.5 EO	22	4.3	-0.6	0.0	38.4	27.3	6.4	13.6	5.8	3.1
Diethanoltallowamide										
plus 3.0 EO	16	3.4	1.5	0.5	37.8	36.5	7.8	14.8	10.4	3.6
plus 5.0 EO	11	6.6	17.5	6.4	37.9	20.0	6.0	17.6	12.4	4.9
plus 10.0 EO	7	7.7	16.9	4.7	39.4	19.0	6.7	18.9	12.2	4.4
Soap only, 0.2%								11.2	-3.0	-2.2

[a]Amount of agent required to keep a lime soap dispersed in 330 ppm hard water. Method of Borghetty and Bergman (8).
[b]Increase in reflectance after washing in the Terg-O-Tometer for 20 min at 120 F.
[c]Cloth A, EMPA; cloth B, Test fabrics Permapress; cloth C, U.S. Testing.
[d]Sodium silicate (SiO_2 /Na_2O) =2;4; also contains 0.002% CMC.

esters and recrystallized to constant melting point as described in an earlier report (5).

The tallow diethanolamide was prepared similarly except for modifications which were needed in order to minimize isomerization of amide to ester. In the case of amides of mixed fatty acids such as tallow fatty acids, the ester cannot be removed by crystallization as in previous preparations of amides of pure fatty acids (6). The synthetic procedure was therefore altered in the following manner: Methyl tallowate was caused to react with a 5% excess of diethanolamine by use of sodium methoxide catalyst. The reaction mixture was heated to 55 C as fast as possible, and heating was continued at 59-63 C for 25 min under a moderate vacuum (10-15 mm Hg) to remove byproduct methanol and excess diethanolamine. The product, which was estimated to contain less than 2% ester by IR analysis, was taken up in boiling hexane, and insoluble soaps were removed by filtration.

γ-Hydroxystearamides

γ-Stearolactone, mp 51.0-51.9 C, was prepared by the isomerization of oleic acid induced by perchloric acid (7). The monoethanolamide of γ-hydroxystearic acid was prepared by heating ethanolamine (0.052 moles) with γ-stearolactone (0.034 moles) neat without catalyst. Reaction began to take place as the lactone melted and was completed as the temperature reached 80 C, 15 min later. Crystallization of the mixture from absolute ethanol at 0 C gave a 98% yield of crude product melting at 98-108 C. Recrystallization from absolute ethanol at room temperature yielded the product (82% yield) which gave the expected IR and NMR spectra; mp 107.7-108.9 C. Analysis: Calculated for $C_{20}H_{41}NO_3$: C, 69.91; H, 12.03; N, 4.09. Found: C, 69.81; H, 12.00; N, 3.99.

The diethanolamide was prepared like the monoethanolamide except for a longer reaction time. After 3 hr of stirring at 105-110 C diethanolamine completely dissolved in the molten stearolactone. The homogenous reaction product, which was a mixture of ester and amide, was allowed to stand at room temperature to favor conversion to the amide. After 5 days the ester content was reduced to less than 10%. The crude product, mp 51.1-53.5 C, was crystallized from a mixture of petroleum ether and absolute ethanol, and isolated in a 94% yield. After two recrystallizations from absolute ethanol a white product was obtained having the expected IR spectra and melting at 66.9-67.7 C. Analysis: Calculated for $C_{22}H_{45}NO_4$: C, 68.16; H, 11.71; N, 3.61. Found: C, 67.74; H, 11.77; N, 3.54.

Oxyalkylations

The Carnes method (4) was used for the oxyethylation of diethanolamides and monoethanolamides.

Twenty grams diethanolamide, 20 ml *t*-butanol and 2 ml triethylamine were placed in a 200 ml stainless steel autoclave, and air was removed by repeated evacuation and flushing with nitrogen. The desired amount of ethylene oxide was distilled into the chilled reaction vessel which was then sealed and placed in a temperature regulated water bath. The mixture was heated at 60 C for 1 hr with magnetic stirring. Subsequently *t*-butanol and amine were removed from the reaction mixture by heating in a rotary evaporator at 60 C under less than 1 mm pressure.

A reaction time of 1.5 hr was required for the oxyethylation of monoethanolamides under the above conditions.

Turbidity Studies

Soap-nonionic solutions having a total concentration of 1% were prepared from sodium oleate and nonionic lime soap dispersing agent, the latter incorporated at levels of 5, 10 or 20%. Two ml of the 1% detergent concentrate and appropriate amounts of 1000 ppm synthetic hard water and

distilled water were mixed to give 10 ml of a 0.2% detergent solution of the indicated hardness.

Turbidity was measured at room temperature (28 C) with a Fisher Electrophotometer II in a 1 cm cell. The dispersions were aged for 1 hr or less depending on the time required to reach a constant turbidity reading. Figures 1 and 2 show the effect of water hardness on turbidity of soap mixed with lime soap dispersing agents of different efficiencies.

Detergent Properties

Lime soap dispersing power was determined by the method of Borghetty and Bergman (8). The values are recorded in Table I as per cent agent (basis soap) required to keep an oleate soap in suspension in 333 ppm hard water.

Detergency was measured in the Terg-O-Tometer operated at 120 F, 110 cycles per minute for 20 min. Five 4 in. circles each of EMPA cotton No.101(A), Testfabrics cotton-polyester with permanent press finish (B), and U.S. Testing cotton (C) cloth were washed in a liter of the indicated solution. Table I shows the results as an increase in reflectance, ΔR, after washing.

RESULTS AND DISCUSSION

Special care was taken to reduce isomerization to ester in the amidation and oxyethylation procedures when working with whole tallow derivatives which were impractical to purify by crystallization. Amidation was carried out at lower temperatures, removing byproduct methanol at reduced pressure. Oxyethylation was carried out at 60 C with a tertiary amine catalyst. The more common procedures, which utilize stronger catalysts and higher temperatures, resulted in partial isomerization to ester and saponification of the diethanolamide.

The effect of esters on the surfactant properties of diethanolamides has long been recognized (9), and it was no surprise to find that these impurities affected lime soap dispersing power and also reduced detergency in combination with soap. A special effort was made therefore to keep ester formation at a minimum so that the products would show optimum surfactant properties. The comparison of various surface active properties described below thus became more meaningful.

Values for lime soap dispersing power of oxyethylated ethanolamides and diethanolamides are listed in Table I and are also plotted as a function of average number of ethylene oxide units in Figure 3. In each case the curve starts at the lowest level of oxyethylation which is required to give water solubility. The single chain compounds made by adding 8 moles of ethylene oxide to ethanolstearamide gave a clear 1% aqueous gel and possessed a Borghetty-Bergman (8) value of 13%. Additional ethylene oxide resulted in products giving more fluid clear 1% aqueous solutions and the lime soap dispersing power increased with further oxyethylation until a value of 3% was attained as 11.2 moles of ethylene oxide were added. The double chain diethanolamide adducts formed a clear gel after the addition of 2.9 moles of ethylene oxide. These adducts possessed a lime soap dispersing power of 12%. With the addition of more ethylene oxide, solubility and lime soap dispersing power improved and reached a value of 2% after a total of 14 moles of ethylene oxide had been added.

Lime soap dispersing power was further investigated by studying turbidity as a function of water hardness. Figure 1 shows turbidity curves for 0.2% total solute solutions containing sodium oleate combined with 5, 10 and 20% of the 4.6 mole ethylene oxide adduct to diethanoltallowamide. These curves resemble those obtained for sodium methyl α-sulfotallowate (2). In the case of the 4.6 mole ethylene oxide adduct to diethanoltallowamide, which

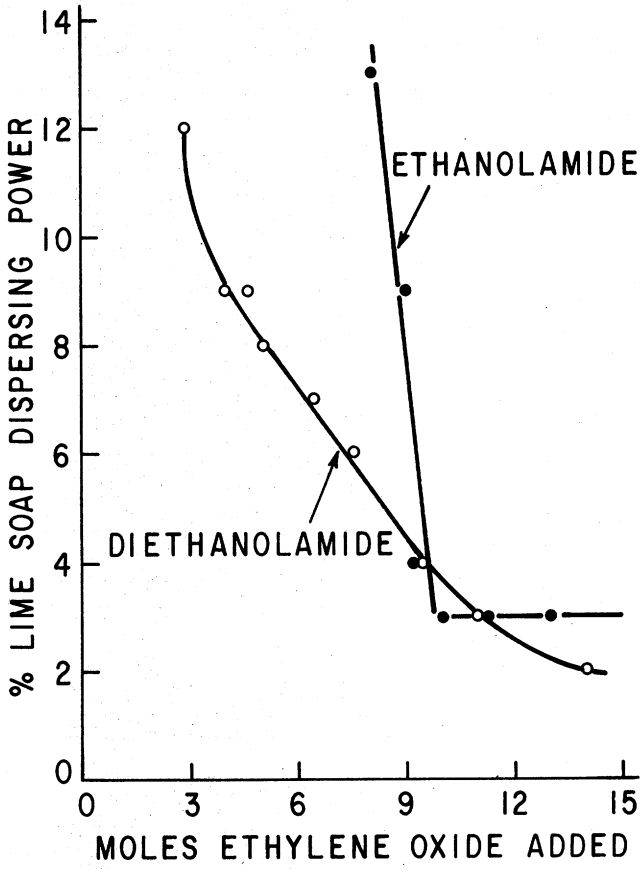

FIG. 3. Effect of oxyethylation on lime soap dispersing power of ethanolamides and diethanolamides.

possesses a comparable lime soap dispersing power, the turbidity curve for the 90% soap–10% nonionic mixture (Fig. 1) was also an almost straight line. Use of the lime soap dispersing agent in soap at a level substantially below the 10% level resulted in precipitation of soap curds, whereas incorporation at a level above 10% resulted in a sharp reduction of turbidity of the soap-nonionic solutions.

Figure 2 shows turbidity curves for the 10 mole adduct to diethanoltallowamide. This adduct has a lime soap dispersing power of 7%. Here a nearly straight line without evidence of precipitation was obtained when only 5% lime soap dispersing agent was added to the soap. However use at higher levels of lime soap dispersing agent exhibited peculiar turbidity maxima just below the stoichiometric point for the reaction of one atom of calcium with two moles of sodium oleate. Beyond this maximum, turbidity returned to the low values expected of more efficient lime soap dispersing agents. It should be noted that the turbidity measurements are highly dependent upon technique and method of addition. Thus the turbidity maxima described above are observed only if the test solutions are prepared by mixing a fixed amount of 1% soap–nonionic solution with a fixed amount of calcium chloride solution. If the technique is altered in such a manner that a slow stream of the calcium chloride solution is added gradually to a well stirred soap-nonionic solution, the above mentioned turbidity maxima are not observed, but instead much straighter turbidity curves are obtained. Coincidence of the maximum near the stoichiometric point for the reaction of calcium ion with soap deserves further study which may lead to an explanation of the nature of soap–lime soap dispersing agent systems.

Table I shows detergency data for diethanolpalmitamides, diethanolstearamides and monoethanolstearamides which have been oxyethylated at different levels. The detergency values (ΔR) were determined for the surfactants alone as well as for soap-surfactant combinations. The soap

formulations contained 64% soap, 21% lime soap dispersing agent and 15% silicate (SiO_2/Na_2O = 2.4). This type of formulation was arrived at somewhat empirically as an outgrowth of formulation studies reported previously (2). Although we observed some exceptions to general patterns, certain trends became evident. Best detergency values, particularly for the combinations with soap, were obtained at the lower levels of oxyethylation. Diethanolamides and monoethanolamides by themselves gave about the same detergency when 11 moles of ethylene oxide was added to either. However the diethanolamides showed better detergency values in combination with soap at lower levels of oxyethylation than the monoethanolamide derivatives. The best detergency results were found for those adducts whose ethylene oxide content was near the minimum required for water solubility. Detergency of all of the soap formulations was reduced when water hardness was increased to 300 ppm, and hard water detergency of these formulations was never as good as that obtained with combinations of soap and anionic lime soap dispersing agents or with phosphate built detergents.

Presence of a hydroxy group in the γ-position of the stearamides increased solubility at low levels of oxyethylation, but did not contribute to the lime soap dispersing power and did not increase the detergency of these ethylene oxide adducts when formulated with soap. Poorer lime soap dispersing power and detergency for the compound derived from γ-hydroxy diethanolamides may be a reflection of shortening the effective hydrophobic chain length below that which is required for a good lime soap dispersing agent.

Although none of the products investigated here were as effective in combination with soap as anionic lime soap dispersing agents, this study demonstrates the advantage of two oxyalkyl chains over a single chain and that a lesser degree of oxyethylation is needed in the case of the twin chains in order to achieve good detergency.

ACKNOWLEDGEMENT

Samples of γ-stearolactone were provided by L.S. Silbert and A. Eisner. Analysis for C, H and N by C. Rzenca and A. Kravitz. P. Pfeffer confirmed the structure of N-2-hydroxyethyl-γ-hydroxystearamide by NMR.

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